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The rates of radical reactions are commonly assumed to be independent of the solvent. We have demonstrated that this assumption is fully justified for hydrogen atom abstraction from cyclohexane by cumyloxy radicals.¹ However, we have also demonstrated the occurrence of dramatic solvent effects on the rates of H-atom abstraction from phenol and *tert*-butyl hydroperoxide by the same radical.² These very large solvent effects were attributed to hydrogen bond formation between the substrate, XOH, and hydrogen bond accepting (HBA) solvents, S. The magnitude of this kinetic solvent effect (KSE) is therefore determined by the strength of the interaction between XOH, the hydrogen bond donor (HBD), and the HBA solvent. This led us to predict that the magnitude of a KSE (i.e., the rate constant ratio, k^A/k^B , measured in two solvents, A and B) would "depend on the Lewis acidity of XOH, (but would) generally be independent of the nature of the radical which abstracts the hydrogen atom".² That is, for the reaction



the ratio of the measured rate constants in solvents A and B will generally be independent of the structure of Y, i.e., $(k^A_{\text{XOH/Y}})/(k^B_{\text{XOH/Y}}) = \text{constant}$ (for the same XOH).

We have confirmed this prediction using phenol and α -tocopherol (vitamin E) as hydrogen atom donating reactants, XOH, and two Y^* radicals having grossly different absolute reactivities in hydrogen atom abstraction.³ The highly reactive Y^* radicals were alkoxyis, cumyloxy (CumO *) in the case of phenol and *tert*-butoxy (BO *) in the case of α -TOH. A single, relatively unreactive Y^* radical was chosen, 2,2-diphenyl-1-picrylhydrazyl (DPPH), because of the ease with which its decay kinetics could be monitored in a conventional spectrophotometer via its strong visible absorption.

Dramatic kinetic solvent effects (KSEs) are shown by the kinetic data in Table 1. For example, the rate constants for abstraction of the phenolic hydrogen atom of α -TOH by DPPH * and by BO * decrease by factors of ~ 67 and ~ 60 , respectively, on changing the solvent from *n*-pentane to γ -valerolactone. Similarly, the rate constants for hydrogen abstraction from phenol by DPPH * and CumO * decrease by factors of ~ 107 and ~ 136 , respectively, on changing the solvent from *n*-octane to ethyl acetate.

These kinetic data in a dramatic fashion confirm our prediction that the magnitude of the KSE on XOH/ Y^* reactions would be essentially independent of the nature of Y^* . Thus, a plot of $\log(k^S_{\text{TOH/BO}}/\text{M}^{-1}\text{s}^{-1})$ vs $\log(k^S_{\text{TOH/DPPH}}/\text{M}^{-1}\text{s}^{-1})$ has most of the points fall very close to the straight line with a slope = 1.0. It is truly astonishing considering that in the same solvent the absolute magnitudes of the two rate constants differ by a factor of over one million. That is, for almost any solvent:

$$k^S_{\text{TOH/BO}}/k^S_{\text{TOH/DPPH}} \approx 1.6 \times 10^6$$

Even more striking are the results with phenol. Once again, the plot of $\log(k^S_{\text{PhOH/CumO}}/\text{M}^{-1}\text{s}^{-1})$ vs $\log(k^S_{\text{PhOH/DPPH}}/\text{M}^{-1}\text{s}^{-1})$ has all but one of the points fall very close to the line drawn with a slope = 1.0. In this set of experiments the absolute magnitudes of the two rate constants in the same solvent differ by a factor of 10 000 000 000! That is,

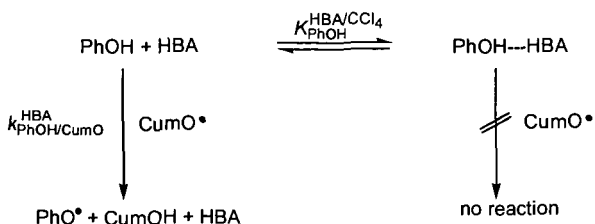
$$k^S_{\text{PhOH/CumO}}/k^S_{\text{PhOH/DPPH}} \approx 1.0 \times 10^{10}$$

Our findings were more recently additionally confirmed with peroxy^{4,5} and carbon-centered⁶ radicals, respectively.

Our studies on kinetic solvent effects (KSE) on free radical reactions have also serendipitously led to a completely new method for measuring equilibrium constants for hydrogen bonding from a variety of XOH to very many hydrogen-bond acceptors

(HBAs) in CCl_4 solvent, $K^{\text{HBA}/\text{CCl}_4}_{\text{XOH}}$. Since this method does not rely on infrared spectroscopy it can also be used to measure $K^{\text{HBA}/\text{CCl}_4}_{\text{XOH}}$ for HBAs containing hydroxylic groups provided only that the hydroxylic hydrogen atom in XOH can be abstracted by free radicals. We demonstrated the validity and simplicity of this new technique using phenol as XOH. Our kinetic measurements yielded $K^{\text{HBA}/\text{CCl}_4}_{\text{PhOH}}$ with HBA's which do not contain OH groups and which serve as a check for our method and $K^{\text{HBA}/\text{CCl}_4}_{\text{PhOH}}$ with HBA's which do contain OH groups, acetic acid, methanol, and *tert*-butyl alcohol.

We suggested a kinetic model² to explain the progressive reduction in the rate of hydrogen atom abstraction from phenol (and *tert*-butyl hydroperoxide) by cumyloxy radicals, CumO^\bullet , as the HBA abilities of the solvents increased. It invoked reactive non-hydrogen bonded XOH and non-reactive hydrogen-bonded XOH, e.g.,



Although we now recognize that this model is oversimplified³ it does yield a very simple and useful kinetic equation, viz.:²

$$k_{\text{PhOH}/\text{CumO}}^{\text{CCl}_4} = k_{\text{PhOH}/\text{CumO}}^{\text{HBA}} (1 + K_{\text{PhOH}}^{\text{HBA}/\text{CCl}_4} [\text{HBA}]) \quad (2)$$

which can be rearranged to

$$\frac{1}{k_{\text{PhOH}/\text{CumO}}^{\text{HBA}}} = \frac{1}{k_{\text{PhOH}/\text{CumO}}^{\text{CCl}_4}} + \frac{K_{\text{PhOH}}^{\text{HBA}/\text{CCl}_4} [\text{HBA}]}{k_{\text{PhOH}/\text{CumO}}^{\text{CCl}_4}} \quad (3)$$

Thus, for *dilute* phenol and HBA in CCl_4 (where their activity coefficients will be unity) a plot of the reciprocal of the rate constant (i.e., $1/k_{\text{PhOH}/\text{CumO}}^{\text{HBA}/\text{CCl}_4}$) measured at 25 °C against [HBA], the concentration of the HBA in CCl_4 , should yield a straight line with an intercept equal to the reciprocal of the measured rate constant in CCl_4 and with a (slope) / (intercept) ratio equal to $K_{\text{PhOH}}^{\text{HBA}/\text{CCl}_4}$. The kinetically derived equilibrium constants for hydrogen bonding between phenol and HBAs are summarized in Table 2 and are compared therein with the ranges of equilibrium constants which have been obtained by the infrared (IR) method at 25 °C.

CONCLUSIONS

We have demonstrated that for hydroxyl hydrogen atom donors rate constants for hydrogen atom abstractions are strongly solvent dependent and independent of the nature of the abstracting radical species. Thus, provided rate constants have been measured for the reaction of one radical with a hydroxyl substrate in a range of solvents, then a measurement of the rate constant for reaction of the same substrate with some different radical need to be made in only one of these solvents for values in all the other solvents to be predicted accurately.

A simplified kinetic model advanced for hydrogen atom abstraction from hydroxyl hydrogen atom donors provides a new method for measuring equilibrium constants for hydrogen bonding from these donors to any hydrogen bond acceptors including alcohols.

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Table 1. Absolute Rate Constants for Abstraction of the Phenolic Hydrogen Atom from α -Tocopherol (TOH) in Various Solvents at 298 ± 2 K

solvent	10^{-8} $k_{\text{TOH/BO}}^{\text{S}}$ ($\text{M}^{-1} \text{s}^{-1}$)	10^{-2} $k_{\text{TOH/DPPH}}^{\text{S}}$ ($\text{M}^{-1} \text{s}^{-1}$)	10^{-7} $k_{\text{PhOH/CumO}}^{\text{S}}$ ($\text{M}^{-1} \text{s}^{-1}$)	10^3 $k_{\text{PhOH/DPPH}}^{\text{S}}$ ($\text{M}^{-1} \text{s}^{-1}$)
	($\text{M}^{-1} \text{s}^{-1}$)	($\text{M}^{-1} \text{s}^{-1}$)	($\text{M}^{-1} \text{s}^{-1}$)	($\text{M}^{-1} \text{s}^{-1}$)
1 <i>n</i> -pentane	99	74		
2 <i>n</i> -octane	60	74	110 ^b	160
3 <i>n</i> -hexadecane	50	73		
4 carbon tetrachloride	42	36	86	93
5 chlorobenzene	36	27	48	59
6 benzene	31	18	28	31
7 anisole	20	14	5.6	7.2
8 acetonitrile	9.4	4.9		
9 acetic acid	7.7	6.2	1.8	3.1
10 methyl acetate	3.0	1.9		
11 ethyl acetate	2.9	1.6 ₅	0.8 ^b	1.5
12 γ -valerolactone	1.6 ₅	1.1		
13 <i>tert</i> -butyl alcohol	1.8	5.7	0.36	2.9

Table 2. Equilibrium Constants for Hydrogen Bond Formation at 25 °C between Phenol and Some Hydrogen Bond Acceptors Measured by the Kinetic Method (Comparison with 25 °C Equilibrium Constants Measured by Infrared Spectroscopy from the Literature)

HBA	[HBA] max (M) ^a	$K_{\text{PhOH}}^{\text{A/CCl}_4}$ (M^{-1})	
		kinetic	infrared (lit)
MeC(O)OH	1.2	1.4	no value
MeCN	0.6	3.5	4.6-6.5
MeC(O)OEt	1.5	6.6	8.8-12.3
MeOH	1.2	11	no value
<i>t</i> -BuOH	0.5	14	44
pyridine	0.3	30	41-53
Me ₂ NCHO	0.17	69	64-76

^aMaximum HBA concentration used to determine the equilibrium constant by the kinetic method.